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ULSAN NATIONAL INSTITUTE OF SCIENCE AND TECHNOLOGY

Master's Thesis

Time-resolved spectroscopic study of dual heteroatom-doped carbon dots

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Graduate School of UNIST

2017

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Time-resolved spectroscopic study of dual heteroatom-doped carbon dots

A thesis/dissertation
submitted to the Graduate School of UNIST
in partial fulfillment of the
requirements for the degree of
Master of Science

Sunghu Kim

12. 15. 2016
Approved by

Advisor
Oh-Hoon Kwon

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Time-resolved spectroscopic study of dual heteroatom-doped carbon dots

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This certifies that the thesis/dissertation of Sunghu Kim is approved.

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Abstract

Carbon dots (CDs) have a potential application in bioimaing due to their excellent photoluminescence (PL), nontoxicity, and excitation-dependent photoluminescence (PL). We studied time-resolved spectroscopic behavior of nitrogen-doped carbon dots (N-CD) and boron-nitrogen doped carbon dots (BN-CD) which were synthesized by one-step microwave pyrolysis. The PL quantum yield of BN-CD was found to be 80.8%, which is approximately twice that of N-CD (40.2%). Although several PL mechanisms of CDs have been proposed in many reports, the origin of the PL of CDs is still in debate. We investigated the origin of the PL of CDs by using a series of spectroscopic methods. The PL lifetimes were fitted by stretched exponential functions which can generally describe to surface-functional PL systems having a distribution of chromophoric states. As a result, we observed that both the CDs pose multiple surface-functional electronic states with a dominant molecular-like state. This study successfully demonstrates the application of stretched exponential functions in describing heterogeneous PL systems.

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Explanation of abbreviations

CDs	- Carbon dots
N-CD	- Nitrogen doped carbon dots
BN-CD	- Boron and nitrogen carbon dots
PL QY	- Photoluminescence quantum yield
CA	- Citric acid
EDA	- Ethylenediamine
XPS	- X-ray photoelectron spectroscopy
TRES	- Time-resolved emission spectra

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Introduction

Carbon nanomaterials such as fullerene,[1] carbon nanotude,[2] graphene,[3] carbon dots (CDs)[4] are promising in nanotechnology due to their unique physical and chemical properties. Carbon dots (CDs) are a new class of the carbon nanomaterials which have commonly below a 10 nm size. CDs generally consist of graphitic structure in few layers and various organic functional groups on the surface of CDs.

CDs have advantages of their unique properties such as excellent photoluminescence (PL), biocompatibility, and high photostability. One of the most advantages of CDs is non-toxicity because heavy metal is not included in CDs as compared with inorganic quantum dots such as CdSe and ZnO.[5-6] In these advantages, CDs can be applied in optoelectronics,[7-8] bioimaing,[9-10] photocatalyst,[11] biosensor,[12] drug delivery[13] and solar light harvesting,[14] *etc.*

The PL quantum yield (PL QY) of CDs is a key parameter for preparing strong fluorescent materials. However, PL QY of CDs is commonly low without chemical modification.[15] So, many studies have been reported to enhance the PL QY of CDs by doping heterogeneous atoms, reduction on the surface, surface passivation, adopting different synthetic conditions and/or using various precursors.[16-22]

The various synthetic routes have been developed in bottom-up and top-down approaches to enhance the performance of luminescence of CDs. The top-down method is a cutting procedure through electrochemical,[23-25] laser ablation,[26-31] and arc charge from bulk carbon materials.[32] The bottom-up process is a synthetic route to build CDs from a small molecule using various organic precursors. The hydrothermal,[33-34] pyrolysis,[17] and microwave-assisted methods[35-36] are generally adopted as the bottom-up process due to the facile synthetic routes. Hongyang Fan & Zaicheng Sun *et al.* reported that the highest PL QY of graphene quantum dots (GQDs) was measured up to 94% through a hydrothermal method using various nitrogen precursors.[16]

As compared to conventional fluorescent dye, CDs have unique optical properties due to their PL depending on excitation wavelengths. To reveal the origin of this phenomenon, many researchers have studied for many years by means of surface passivation,[9-10, 17, 37-38] adopting different synthetic methods,[39-40] changing synthetic conditions,[20, 41-42] pH,[43-45] and chemical reduction,[46-47] etc. However, the origin of the PL of the CDs is still debated in current status. The several mechanisms of the PL behaviors of carbon materials including CDs have been proposed; abundant chemical functional

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groups on the CDs surface,[41, 48-49] quantum confinement effects,[29, 50-51] electron-hole localized states due to the oxygen-related functional groups,[47, 52] and molecular-like state,[37, 39, 42, 53-54] *etc*. Bhattacharya *et al*. observed that CDs show the wide size distribution from AFM profile.[50] They concluded that an excitation-dependent PL behavior of CDs originates from the quantum confinement effect rather than the distribution of different surface trap states. Pang *et al.* prepared CDs with different degree of surface oxidation by electrochemical method.[41] They suggested that the excitation-dependent PL of CDs was attributed to the oxygen-related surface states. Yang *et al.* prepared CDs by a hydrothermal route using a citric acid and ethylenediamine (EDA) as the precursors.[54] They observed that the fluorescent molecules (imidazo[1,2-*a*]pyridine-7-carboxylic acid, 1,2,3,5-tetrahydro-5-oxo-, IPCA) were found to be in CDs. They suggested that IPCA molecules which are called to the molecular states contribute the strong blue emission of CDs.

Here, we synthesized the boron-and-nitrogen co-doped CDs (BN-CDs) thorough a single-step microwave route using citric acid (CA), ethylenediamine (EDA), and boric acid as the precursors.[15] BN-CD has a novel type of dual heteroatom-doped carbon dots which have high photostability and excellent PL as compared with plain carbon dots (CDs) and nitrogen-doped carbon dots (N-CDs). The PL QY of BN-CD (80.8%) is twice as compared to that of N-CD (40.2%) due to having their different nitrogen configuration.[15] Aforementioned, the photoluminescence mechanism is still open debate. We analyzed the series of spectroscopic results by using X-ray photoelectron spectroscopy (XPS), UV-vis spectroscopy, photoluminescence (PL) and time-resolved electronic spectroscopy to reveal the origin of photoluminescence mechanism. We also suggested that the CDs have mainly two components of PL with the heterogeneous systems (multiple electronic states) and a dominant homogeneous system (molecular-like state) according to a stretched exponential function.

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Methods and Materials

Nitrogen-doped carbon dots (N-CD) have synthesized microwave pyrolysis routes which performed in presence of a citric acid and EDA as the precursors. Boron and nitrogen doped carbon dots (BN-CD) are also prepared by a microwave pyrolysis method in presence of a citric acid, an ethylenediamine, and a boric acid as the precursors. Both CDs are prepared by Dr. Yuri Choi.[15] The structural analysis of CDs was obtained using a X-ray photoelectron spectroscopy (K-alpha, Thermo Fisher), these data were also measured by Dr. Yuri Choi.[15] UV-vis spectra were obtained by using a UV-vis spectrometer (V-730, Jasco) and steady-state fluorescence spectra were obtained by using a fluorometer instrument (Shimadzu 6000). PL lifetimes were measured by a time-correlated single photon counting spectrometer (Fluotime 300, PicoQuant) with the light source of picosecond-pulsed diode lasers emitting at 375 nm (LDH-D-C-375, PicoQuant). The total instrument response function (IRF) was ~190 ps. All fluorescence decay profiles were fitted to stretched exponential function exponential functions by using the software (FluoFit, PicoQuant) to deduced fluorescence lifetimes.

Results and Discussion

1. Steady-state absorption and emission spectra

The optical characterization of both the CDs was investigated in this study (**Figure 1**). Absoption peaks were found to be at ~250 nm and ~350 nm in both CDs which are generally assgined to π-π^* and n-π^* transition corresponding to the sp^2 carbon core transition and the transition of the surface functional groups, respectively.[16, 19, 37, 53, 55-56] In addition, nitrogen doped carbon dots (N-CD) absorb the light over the visible range at ~420 nm, indicating of presence of multiple electornic states whereas there is no absorption tail in boron-nitrogen doped CDs (BN-CD). The PL maximum of both CDs features at ~450 nm with excitation at 350 nm, and their PL excitation spectrum also found to be at ~250 and ~350 nm under emission wavelength at 450 nm. Inset shows the PL spectrum with weak shoulder at ~330 nm under excitation at 250 nm which is related to transition of carbon core. The reason that PL intensity at ~330 nm is very weak as compared to the peak at ~450 nm maybe due to the energy transfer. The PL spectra of N-CD showed an excitation-dependent behavior due to having the multiple electronic states on the surface of CDs (**Figures 2a, S1a**). The PL excitation spectra of N-CD found to be at ~250 nm, ~360 nm, ~450 nm, and ~510 nm (**Figures 2b, S1b**). However, the maximum of the PL of the BN-CD was centered at ~450 nm which was independent on excitation wavelengths in contrast to that of N-CD (**Figures 3a, S2a**). In addition, the PL excitation spectra of BN-CD feature the bands at ~250 nm and ~350 nm (**Figure 3b, S2b**). These bands were also found in N-CD, whereas the bands at ~450 nm and ~510 nm were suppressed in BN-CD. In basis of our results, the bands over the visible range at ~450 nm in PL excitation spectra lead to an excitation-dependent

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PL behavior. As our best knowledge, the excitation-dependent PL of CDs is generally accepted due to the oxygen-related surface functional groups which can form multiple electornic states.[17, 41]

2. X-ray photoelectron spectroscopic measurement

To analyze of the chemical compositions of both the CDs, X-ray photoelectron spectroscopy (XPS) were peroformed (**Figure S4**). The major elements of both CDs consisted C, N, and O. In the high resolution C 1s spectra, the fractions of carbon-related bonding with N and O species were different between N-CD and BN-CD. The fit results were summarized in BN-CD: C=C (284.74 eV), C=O (287.92 eV), C-N (285.77 eV) and COOH (288.79 eV). As compared to N-CD, the fractions of C=C and C=O were increased whereas that of COOH and C-N were reduced in BN-CD. Interestingly, the N 1s spectra show the different nitrogen configurations between N-CD and BN-CD. N-CD possess dominantly pyrrolic-N, whereas the BN-CD mainly consists of graphtic-N. On the basis of these results, the nitrogen configurations play important role of their PL behaivor. We suggest that the pyrrolic-N caused the formation of the nitrogen-related defect states, however, the graphtic-N enhanced the conjugation of sp^2-related carbon domains. Zou *et al.* also suggested that the nitrogen defect can form the absorption tail over the visible range at ~450 nm and excitation-dependent PL.[57] Therefore, the PL QY of BN-CD (80.8%) is nearly twice as compared to that of N-CD (40.2%).[15]

3. Time-resolved spectroscopic analysis

We obtained time-resolved PL decay profiles of both the CDs using a time-correlated single photon counting (TCSPC). The PL decay transients of N-CD show more dependent PL decay time with monitored wavelengths as compared to those of BN-CD (**Figure 4**). In other words, the PL decay time was shortened as increasing the emission wavelength due to their emissive states on the surface of CDs, whereas the PL decay time of BN-CD is independent on emission wavelengths that means the surface electronic states of BN-CD is less having than that of N-CD. We investigated to deeply understand the origin of the PL of both the CDs, all decay curves were fitted by multiple stretched exponential functions as following equation.

$$I(\mathrm{t}) = \sum_{i=1}^{n} A_i \exp(-\frac{t}{\tau_i})^{\beta_i}$$

The stretched exponential function is commonly used for disordered relaxation systems which are introduced in CDs due to their complicated luminophores. Here, we presented the stretched exponential decay parameters; PL lifetimes (τ), fractional amplitudes of fluorescence lifetime components and β which is distribution of PL lifetimes where a smaller β means a wider distribution of PL lifetimes (**Tables 1,2**). According to the stretched exponential parameters in N-CD, the PL

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lifetimes were found to be 12-15 ns (τ_1) and 500 ps-3 ns (τ_2) which correspond the values of β with ~1.0 (β_1) and 0.5-0.8 (β_2), respectively. The PL lifetimes in BN-CD are also obtained to be ~15 ns (τ_1) and 400 ps-2 ns (τ_2) which presented the values of β with ~1.0 (β_1) and ~0.3 (β_2), respectively. The fractional amplitudes of τ_1 are dominant at 450 nm in both CDs which found to be 0.76 and 0.93 in N-CD and BN-CD, respectively. As increasing the emission wavelength, the fractional amplitude of τ_1 is decreased and that of τ_2 increased in both the CDs. The PL lifetimes of τ_1 are similar between N-CD and BN-CD. The PL lifetimes of τ_1 were already reported to the lifetime of IPCA molecule.[54] *Nann et al.* also reported that the fitting of PL lifetimes of graphene quantum dots were mainly found two systems, a homogeneous with fluorescein dye and a highly heterogeneous system.[58] The values of other PL lifetimes (τ_2) in both CDs are varied with the emission wavelengths and the values of β are also smaller than 1.0 that means these components originate from heterogeneous electronic systems. We suggest that heterogeneous electronic systems come from surface functional groups of the CDs. As the basis of the results, the molecular states dominantly contribute their strong blue emission and the surface fucntional groups can form disordered electronic states of the CDs.

To find the emitting species of the CDs, we obtained time-resolved emission spectra (TRES) from 400 to 650 nm with 5-nm incretments. The spectral maximum is found at ~450 nm in both the CDs with excitation at 375 nm (**Figures 5a, 6a**). In time-resolved area normalized spectra (TREANS), there were neither spectra shifts nor isoemissive points at varing time delays in both the CDs (**Figure S3**).

All kinetic profiles at λ_{em} = 400-650 nm were also fitted by multiple stretched exponential functions in both the CDs. The distribution of fitting parameters with amplitudes of each PL lifetime component (A_i), distribution of PL lifetimes, β_i, and their PL lifetimes (τ_i) are given in the whole range of wavelengths (400-650 nm) in both the CDs (**Figures 5b-d, 6b-d**). A_1 is found to be at ~450 nm and it has dominant contribution in both the CDs. This amplitude in both the CDs corresponds the values of β_1 and τ_1 with ~15 ns and ~1.0, respectively. The dominant amplitude originates from molecular states because this component matches well the PL lifetime of the IPCA and homogeneous systems (β_1 = ~1.0). On the other hand, the contribution of A_2 is more dominant in N-CD as compared to that of BN-CD. Futhermore, the N-CD has the values of β_2 at ~0.6 and disordered distribution of the PL lifetimes in the whole range of wavelengths. However, the BN-CD has the values of β_2 at ~0.3 and well distributed PL lifetimes at ~400 ps. According to these results, the values of β_2 are smaller in BN-CD whereas the PL lifetimes with τ_2 are more randomly distributed in N-CD. Interestingly, the values of β_1 and τ_1 are slightly disordered only in N-CD at the longer wavelengths from ~550 nm. However, These values are constant in BN-CD at the whole range of wavelengths. We suggest that the disordered PL lifetimes are due to multiple chemical chromophores on the surface of CDs and the

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values of β mean the distribution of the relaxation chennels on each chemical chromophore. According to our proposed PL mechanism, Although the BN-CD has less chemical chromophores as compared to that of N-CD, BN-CD has more relaxation chennels on each chemical chromophore than that of N-CD. The reason of having variable realxation chennels in BN-CD is due to local enviroment effect on their chemical chromophores which maybe originate from the conjugation systems on the carbon core, surface electronic localized states, sp^3 carbon defect and so on.

Our summarized PL mechanism of both the CDs is shown (**Scheme 1**). Carbon core domains are excited at ~250 nm, and their emission at ~330 nm which is very weak due to the fast energy trasnfer to a dominant molecular state. The maximum of molecular states is found to be ~450 nm and their absorption at ~350 nm. The PL lifetime is estimated to be ~15 ns at ~450 nm in both CDs, and the lifetime is well defined (β = ~1.0) as that of IPCA. The surface states are exicted above 420 nm and their PL is dependent on chemical chromophoric states The absorption tail featured only N-CD beyond the ~420 nm and excitation spectra show the bands at ~450 nm and ~510 nm. N-CD has the various PL lifeitmes (~200 ps-3 ns) on surface of CDs that means the multiple chemical chromophoric states and results in excitation-dependent PL. On the other hand, BN-CD has the well distributed PL lifetimes (~400 ps) on the surface of CDs that means having less surface chemical chromophores. The well distributed PL lifetimes lead to the excitation-independent PL behaivor. Instead, the values of β are smaller in BN-CD as compared to that of N-CD. We suggest that the BN-CD has more relaxation chennels on each chemical chromophore as compared to that of N-CD. According to the chemical composition of the CDs, N-CD has dominant functional groups with –COOH and pyrrolic-N whereas the BN-CD pose abudant function groups with graphtic-N. The fucntional groups of –COOH and pyrrolic-N form the multiple chemical chromophores which lead to the excitation-dependent PL haviors. We conclued that the chemical composition on the surface of CDs can affect the excitation-dependent PL behaivor.

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Conclusion

In summary, the PL mechanisms of the CDs have been proposed with various points of view for few years. However, the origin of the PL of the CDs is still debated and unclear. We investigated the PL mechanism of the CDs by analyzing the series of spectroscopic measurements with steady-state absorption and emission spectra, time-resolved PL, and using a X-ray photoelectron spectroscopy (XPS). The PL behavior of N-CD is dependent on excitation wavelengths whereas that of BN-CD is independent on excitation wavelengths. We observed that the different nitrogen configuration between N-CD and BN-CD is a key role of an excitation-dependent PL behavior and results in their different values of PL QY. To deeply understand their PL mechanisms, the PL lifetimes of both the CDs were fitted by stretched exponential fucntions due to their complicated electronic states. CDs pose the two electronic states which are homogeneous PL system and heterogeneous PL system with a dominant molecular-like state and multiple surface functional electronic states. Molecular-like states dominantly affect their strong blue emission with PL lifetime at ~15 ns which correspond to the PL lifetime of IPCA. The multiple surface fucntional electronic states contribute their excitation-dependent PL behaviors. We believe that this study will help understand the origin of the PL of carbon nanomateirals in future perspective.

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Figures, Schemes and Tables

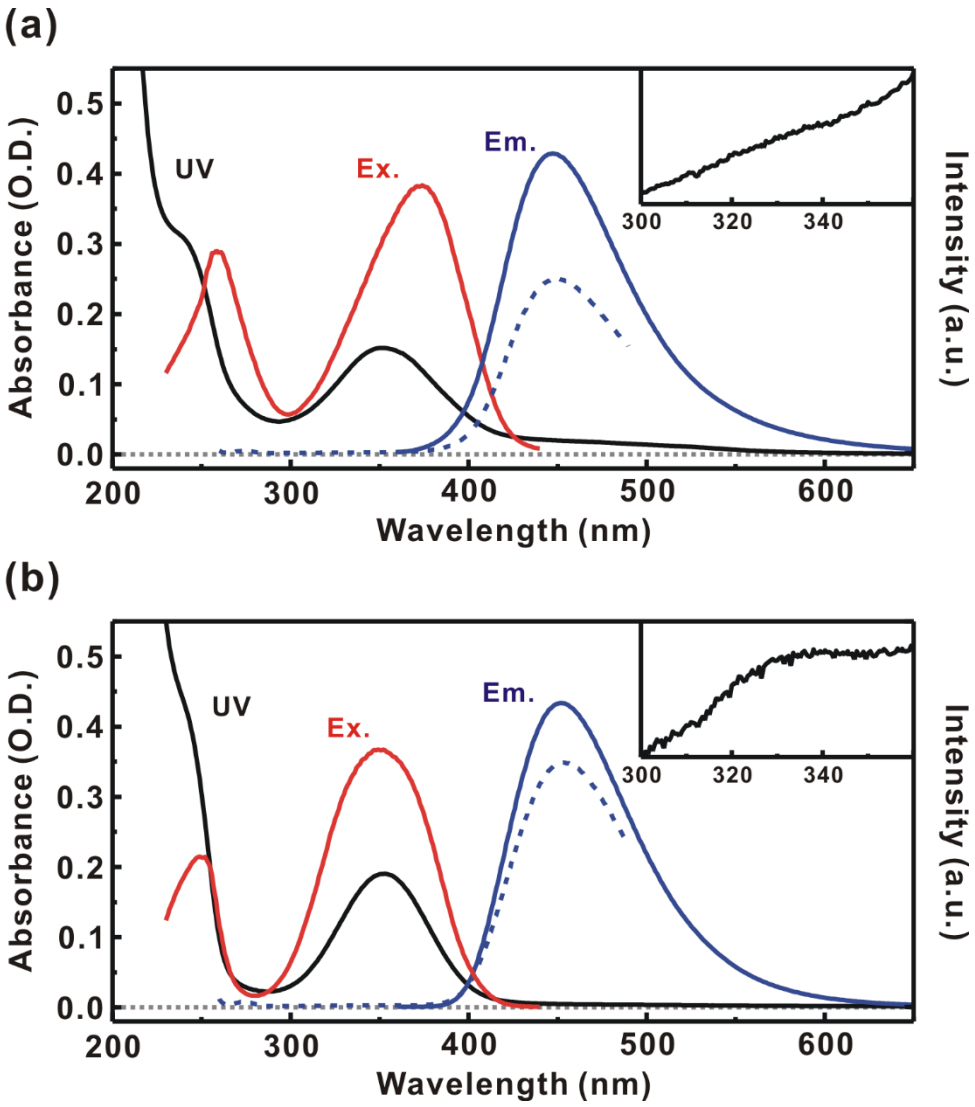

Figure 1. Optical spectra of CDs in an aqueous solution. Absorption spectrum (black solid line), excitation spectrum (red solid line), and PL spectra (blue solid and dashed line) of (a) N-CD and (b) BN-CD. Emission spectra were measured by excitation at 250 nm (blue dashed line) and 350 nm (blue solid line). Excitation spectra were measured by emission at 450 nm. Insets show the magnified PL spectra with excitation at 250 nm.

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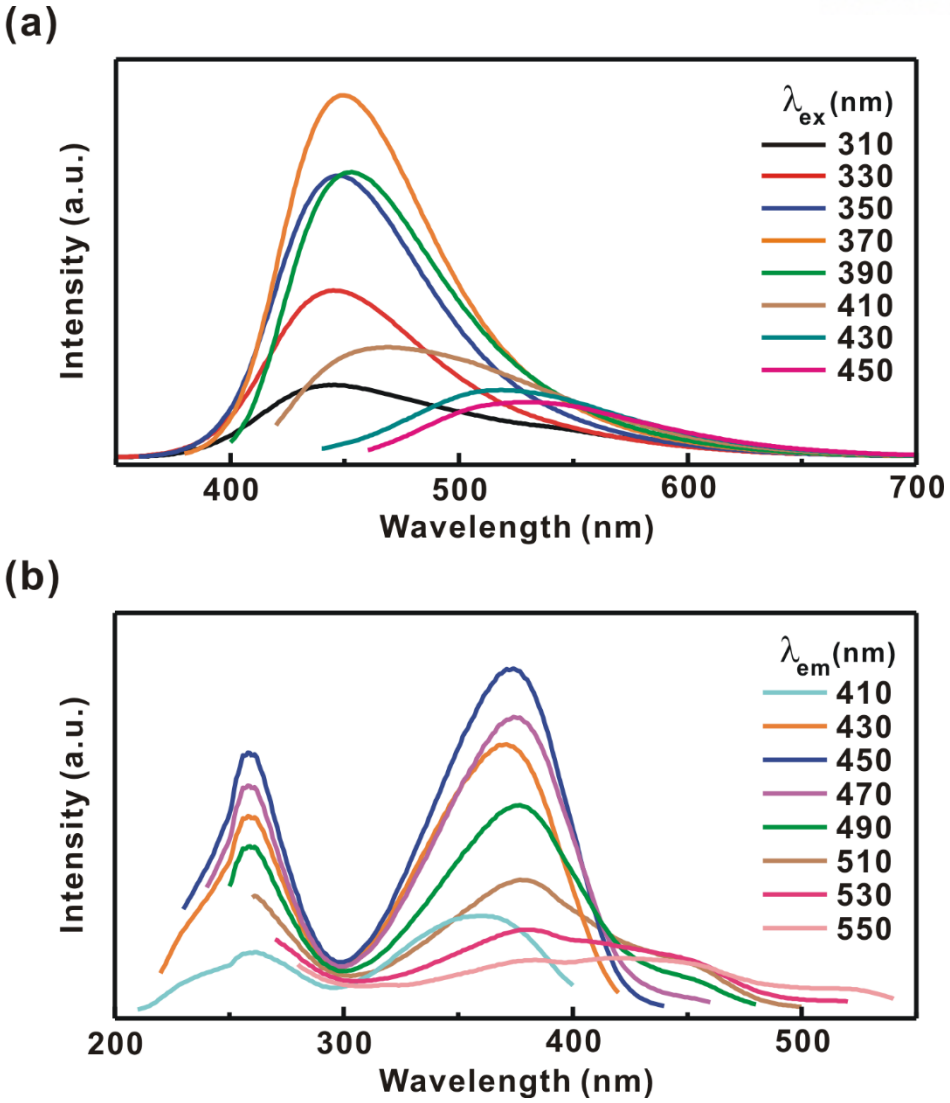

Figure 2. (a) PL spectra of N-CD with varying excitation wavelengths from 310 to 450 nm with 20 nm increments. (b) Excitation spectra of N-CD with varying emission wavelengths from 410 to 550 nm with 20 nm increments.

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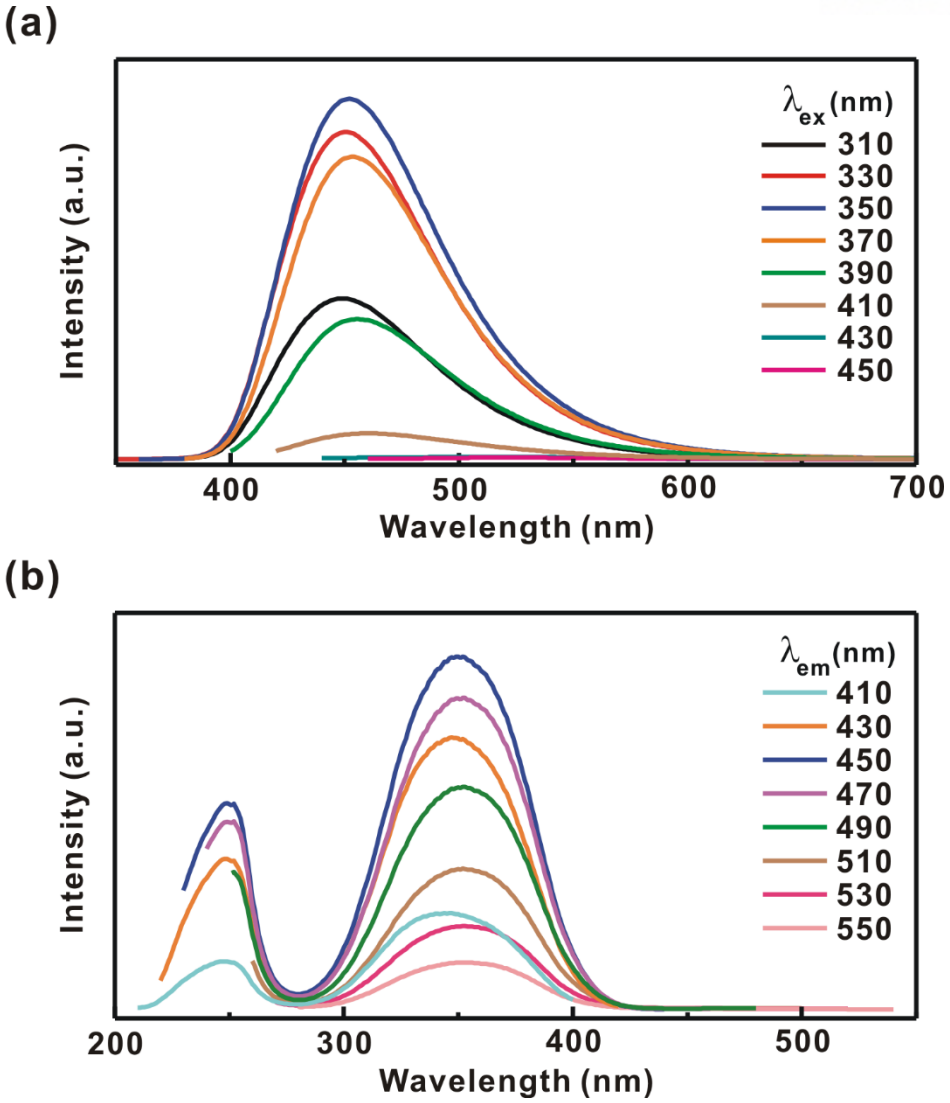

Figure 3. (a) PL spectra of BN-CD with varying excitation wavelengths from 310 to 450 nm with 20 nm increments. (b) Excitation spectra of BN-CD with varying emission wavelengths from 410 to 550 nm with 20 nm increments.

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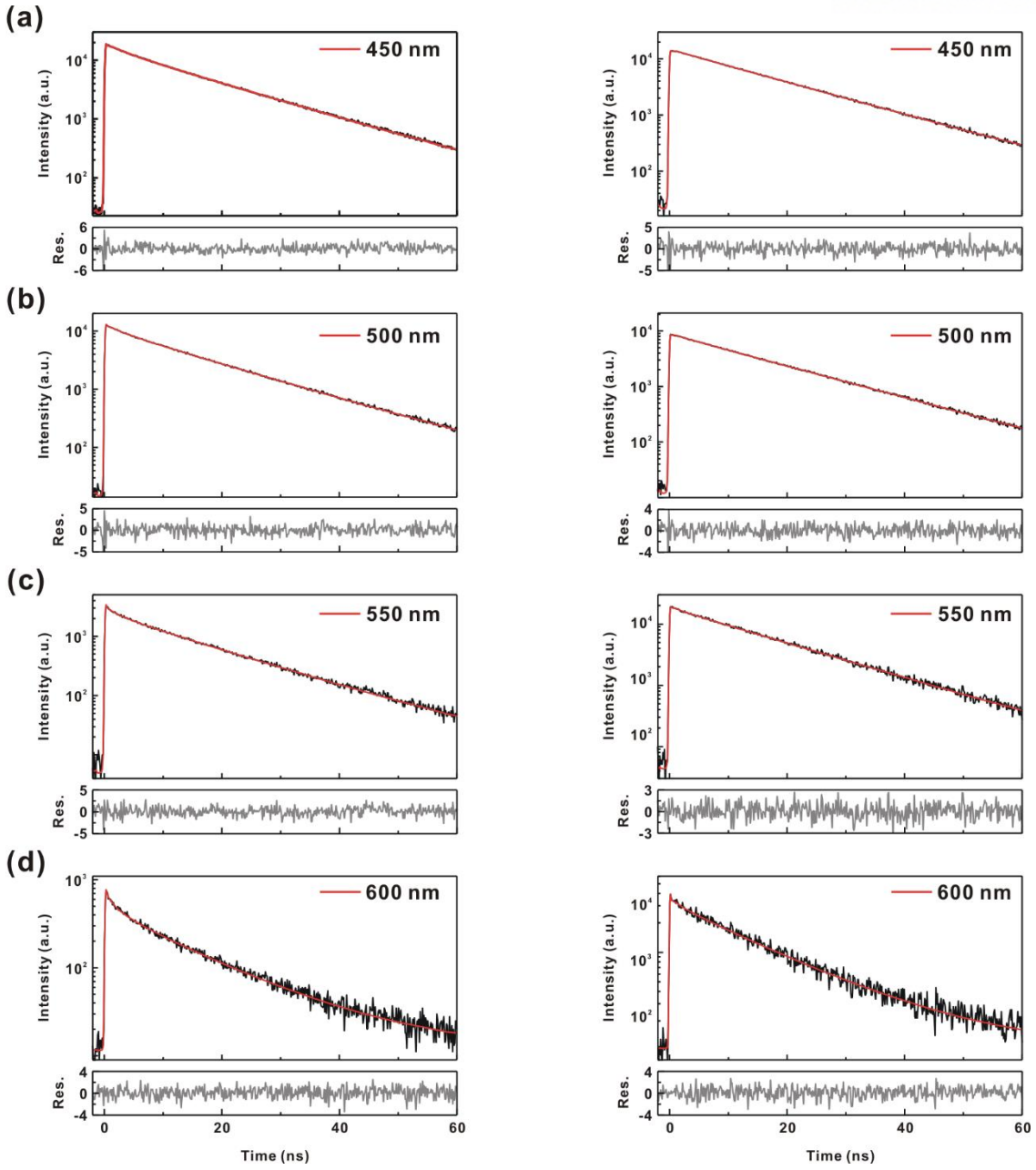

Figure 4. Fluorescence decay profiles of N-CD (left panels) and BN-CD (right panels) with excitation at 375 nm monitored at (a) 450 nm, (b) 500 nm, (c) 550 nm, and (d) 600 nm, respectively.

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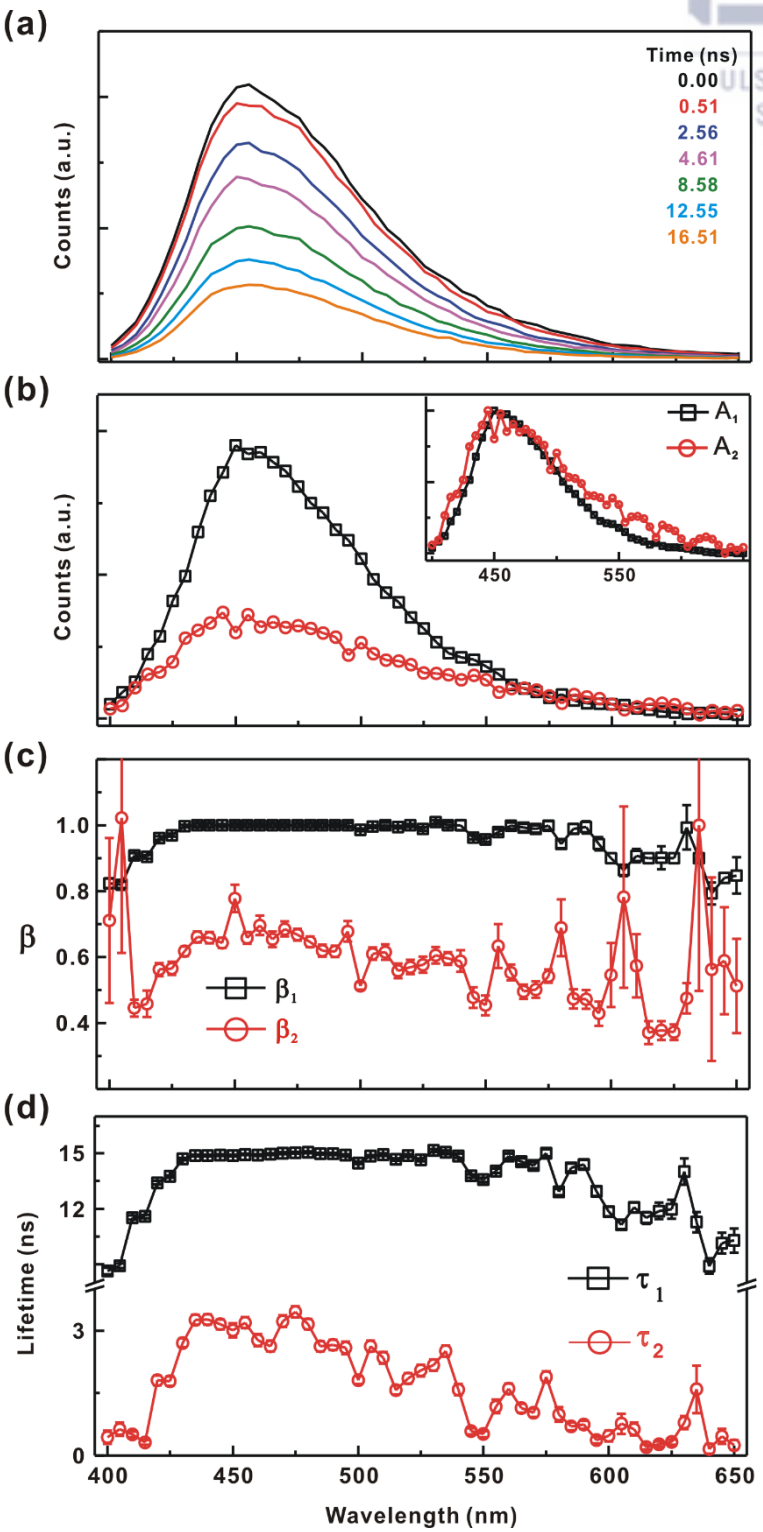

Figure 5. (a) Time-resolved emission spectra (TRES) of N-CD with excitation wavelength at 375 nm. Fitting parameters are given according to stretched exponential functions (b-d). (b) The amplitudes of fluorescence lifetime components of N-CD. (c) Stretched exponential distribution factor, β, of N-CD. (d) Fluorescence lifetimes of N-CD. All decay transients were taken from 400 to 650 nm with 5 nm increments. Inset shows the normalized spectra.

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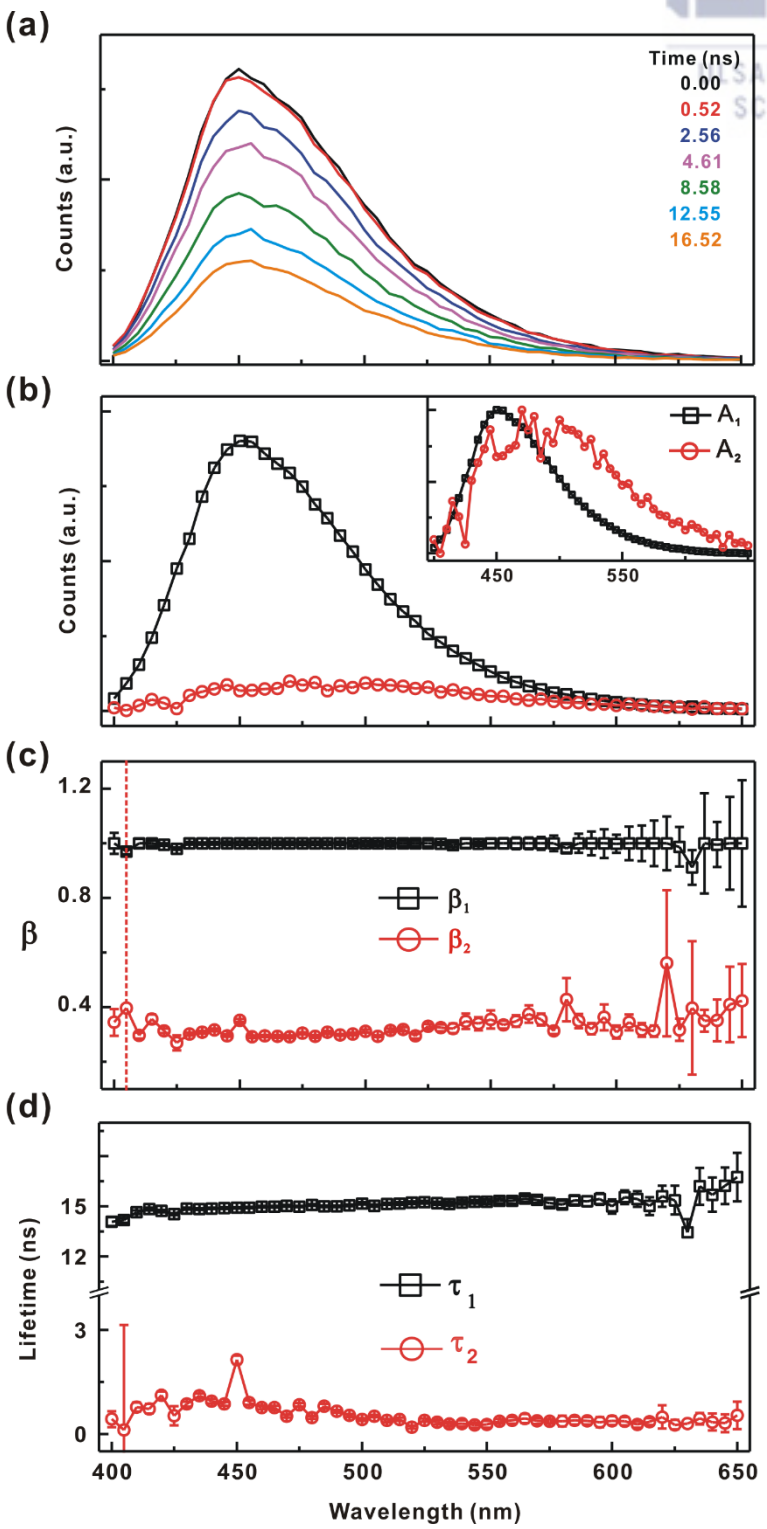

Figure 6. (a) Time-resolved emission spectra (TRES) of BN-CD with excitation wavelength at 375 nm. Fitting parameters are given according to stretched exponential functions (b-d). (b) The amplitudes of fluorescence lifetime components of BN-CD. (c) Stretched exponential distribution factor, β, of BN-CD. (d) Fluorescence lifetimes of BN-CD. All decay transients were taken from 400 to 650 nm with 5 nm increments. Inset shows the normalized spectra.

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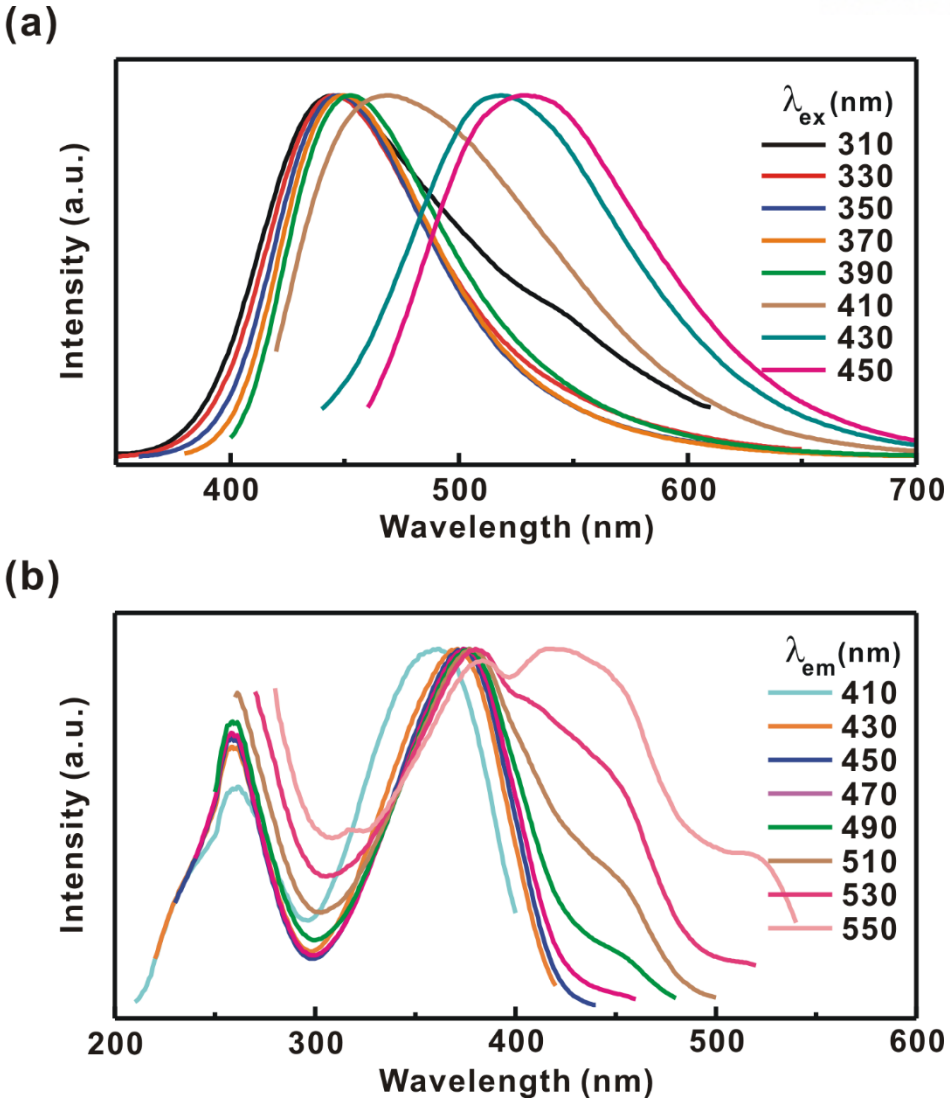

Figure S1. (a) Normalized PL spectra of N-CD with varying excitation wavelengths from 310 to 450 nm with 20 nm increments. (b) Normalized excitation spectra of N-CD with varying emission wavelengths from 410 to 550 nm with 20 nm increments.

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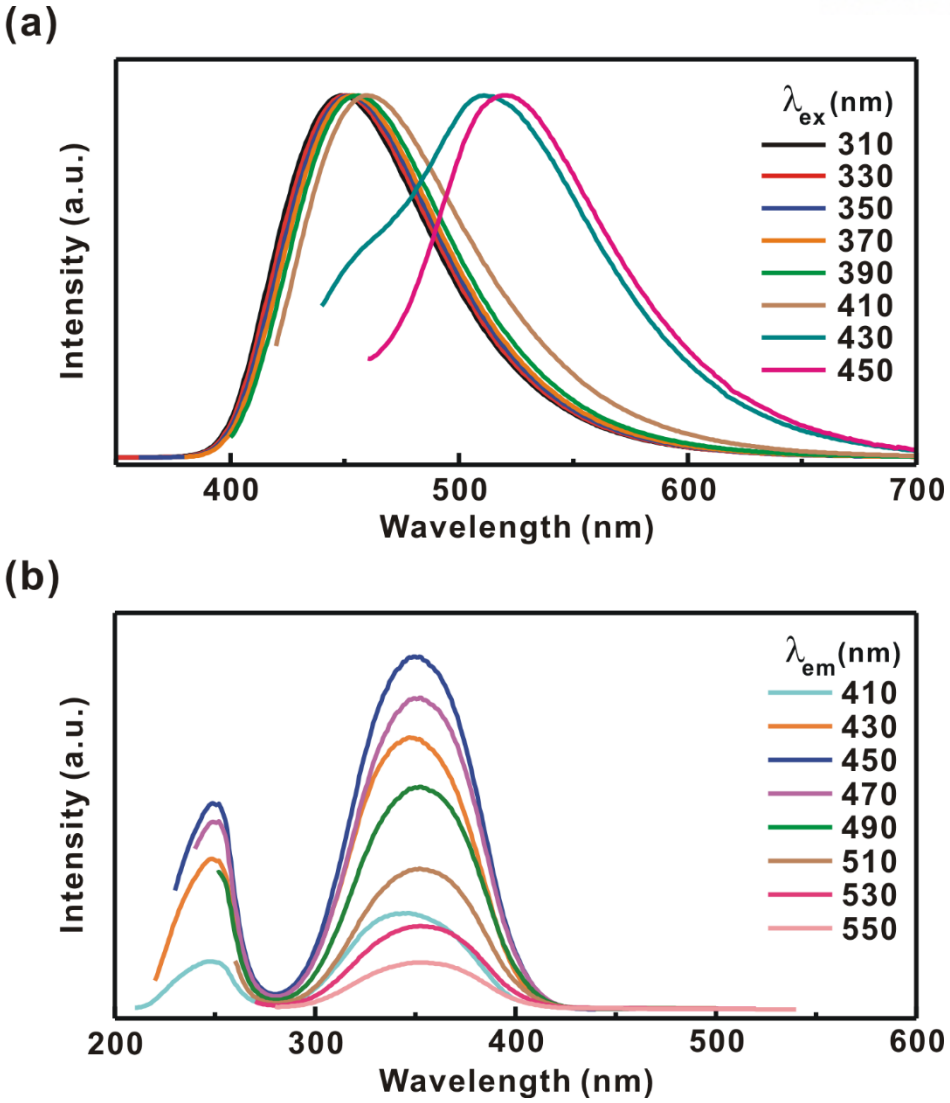

Figure S2. (a) Normalized PL spectra of BN-CD with varying excitation wavelengths from 310 to 450 nm with 20 nm increments. (b) Normalized excitation spectra of BN-CD with varying emission wavelengths from 410 to 550 nm with 20 nm increments.

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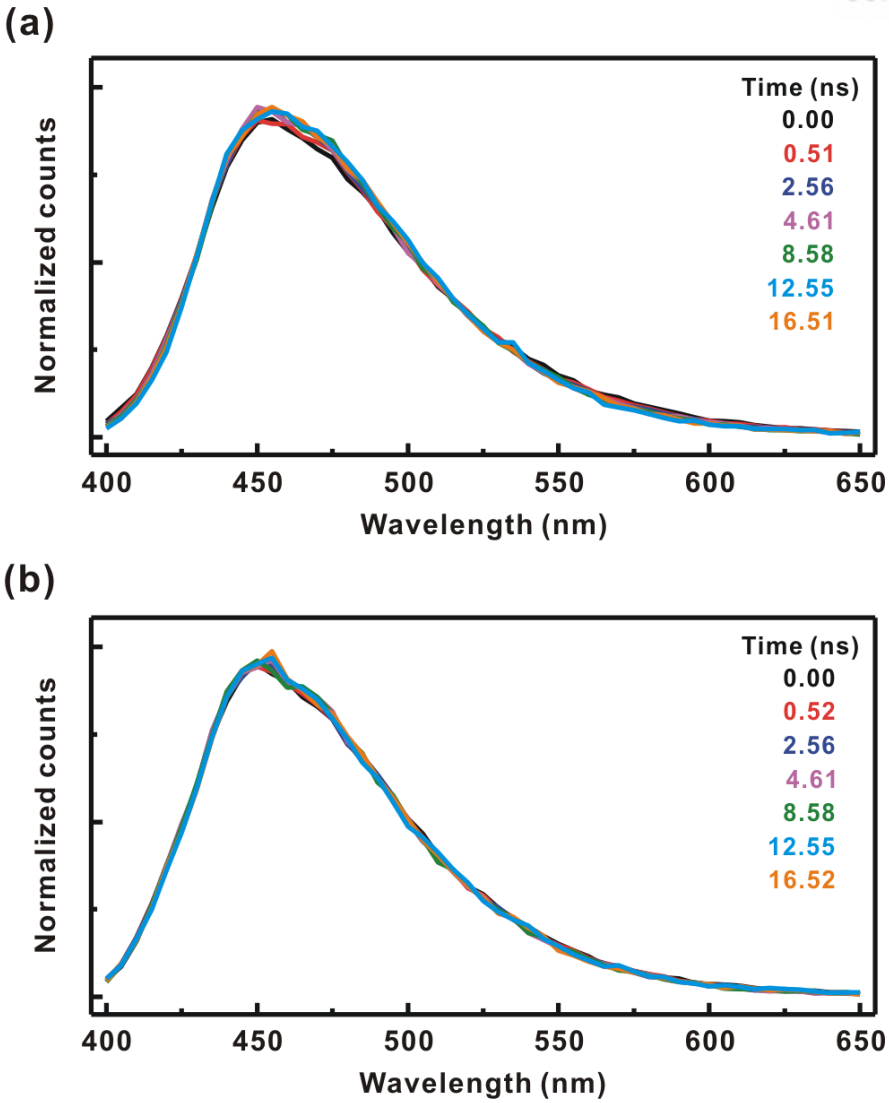

Figure S3. Time-resolved area normalized emission spectra (TRANES) of (a) N-CD and (b) BN-CD.

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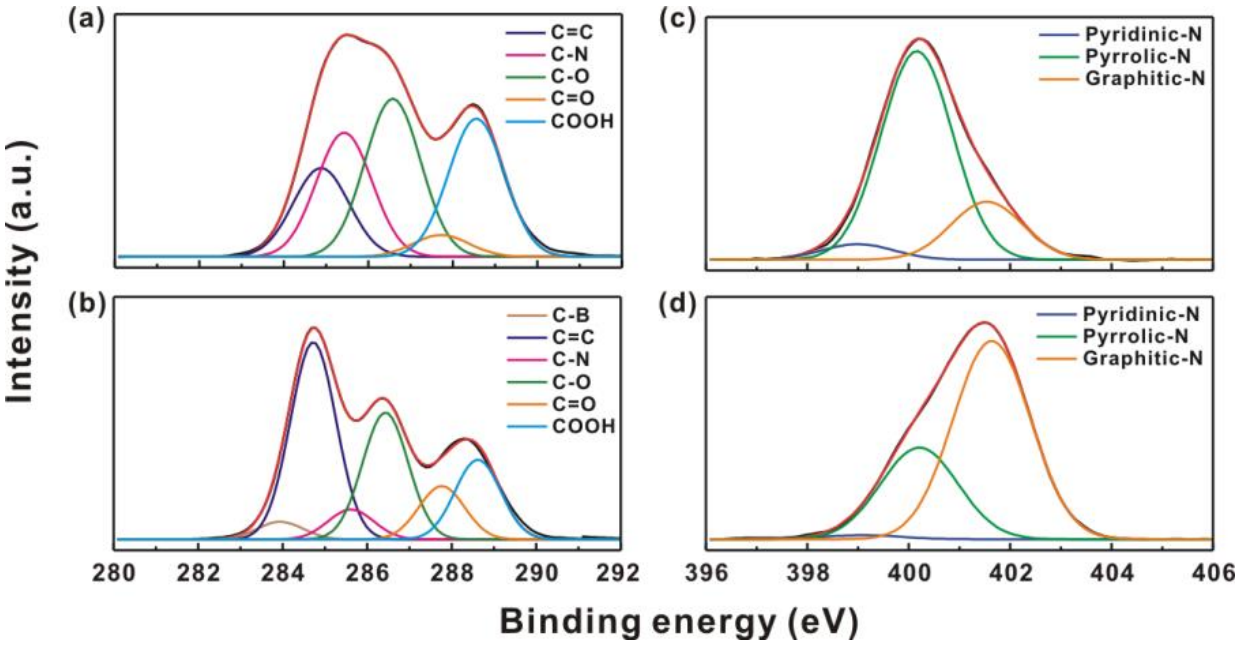

Figure S4. High-resolution XPS spectra C 1s and N 1s of (a,c) N-CD and (b,d) BN-CD, respectively.

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Table 1. Fitting parameters of PL decay of N-CD with excitation at 375 nm.

N-CD					
λ_{em} (nm)	τ_1 (ns)	β_1	τ_2 (ns)	β_2	χ^2
450	14.87 ± 0.05 (76%)[a]	1.00[b]	3.01 ± 0.17 (24%)	0.78 ± 0.04	1.284
500	14.48 ± 0.06 (68%)	0.99	1.81 ± 0.09 (32%)	0.51 ± 0.01	1.212
550	13.57 ± 0.11 (57%)	0.96 ± 0.01	0.52 ± 0.08 (43%)	0.45 ± 0.03	1.041
600	11.85 ± 0.25 (50%)	0.90	0.47 ± 0.13 (50%)	0.55 ± 0.10	0.929

[a]**Fractional amplitude with PL lifetime.**

[b]**Distribution parameter according to stretched exponential function.**

Table 2. Fitting parameters of PL decay of BN-CD with excitation at 375 nm.

BN-CD					
λ_{em} (nm)	τ_1 (ns)	β_1	τ_2 (ns)	β_2	χ^2
450	14.90 ± 0.05 (93%)[a]	1.00 ± 0.01[b]	2.14 ± 0.13 (7%)	0.35 ± 0.01	1.289
500	15.17 ± 0.06 (83%)	1.00 ± 0.01	0.42 ± 0.04 (17%)	0.31 ± 0.01	1.071
550	15.27 ± 0.13 (73%)	1.00 ± 0.01	0.28 ± 0.10 (27%)	0.36 ± 0.03	1.000
600	14.99 ± 0.43 (62%)	1.00 ± 0.03	0.38 ± 0.13 (38%)	0.31 ± 0.02	1.033

[a]**Fractional amplitude with PL lifetime.**

[b]**Distribution parameter according to stretched exponential function.**

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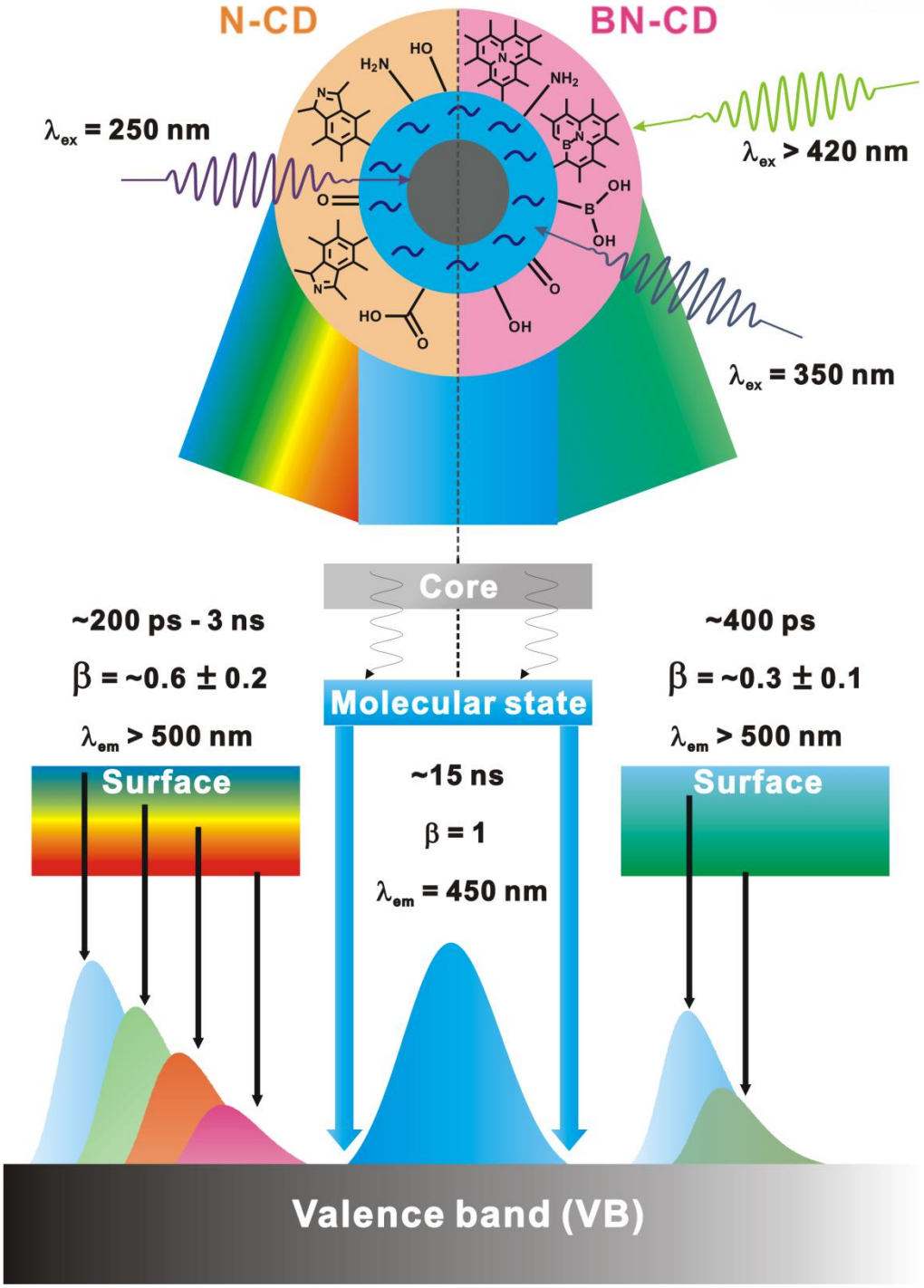

Scheme 1. Proposed PL mechanism of both CDs.

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